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SHORT COMMUNICATION

CHEMIEXCITATION OF AN ANTHRAQUINONE DERIVATIVE IN THE THERMAL CYCLOREVERSION OF A DEWAR-ANTHRAQUINONE DERIVATIVE

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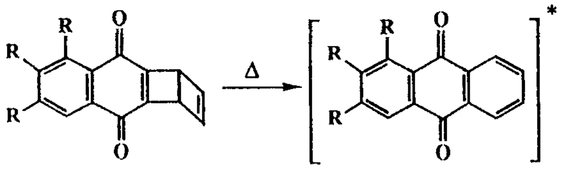
Dewar-anthraquinone (1a) and 1,2,3-tri-*tert*-butyl-5,8-Dewar-anthraquinone (1b) were synthesized. Thermodynamic parameters for their cycloreversion to the corresponding anthraquinones indicate that thermal population of the excited states of the products via non-adiabatic valence isomerization is energetically feasible. On thermolysis of 1b, the formation of a detectable amount of 1,2,3-tri-*tert*-butyl-1,4-Dewar-anthraquinone (3) was observed. The excited singlet state of 1,2,3-tri-*tert*-butylanthraquinone (2b) produced via the non-adiabatic process is responsible for the formation of 3.

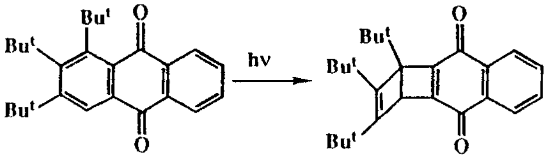
The formation of excited triplet benzene in the thermolysis of Dewar-benzene reported by Lechtken *et al.*[1] is the prototype and rare example of a simple unimolecular chemiexcitation. In a study of light energy storage based on the photosynthesis of strained molecules,[2] we were interested in this intriguing class of non-adiabatic valence isomerization as a type of releasing strain energy. In this connection we have now studied the chemiexcitation in the thermal cycloreversion of 1,2,3-tri-*tert*-butyl-5,8-Dewar-anthraquinone (**1b**) to 1,2,3-tri-*tert*-butylanthraquinone (**2b**) [equation (1)].



1 **2***

a; R = H
b; R = t-Bu (1)

The thermal reaction of **1b** to **2b** possesses the following characteristic features: (i) both the S_1 and T_1 states of the product, **2b**, possess a lower energy than the transition state for the thermal isomerization; and (ii) on excitation, **2b** affords 1,2,3-tri-*tert*-butyl-1,4-Dewar-anthraquinone (**3**) as shown in equation (2).[3]



2b **3**

(2)

The former feature also occurs in the reaction of Dewar-acetophenone to acetophenone.[4] However, the present system, **1b**–**2b**, possesses fundamentally different features from the Dewar-acetophenone reaction as follows. In the case of the chemiexcitation in the isomerization of Dewar-acetophenone to acetophenone, the key bond-breaking and -making process is located on the benzene moiety whereas the final excited states ($n\pi^*$) are localized on the carbonyl moiety. Turro *et al.*[4] attributed the low efficiency of excited state production by the thermolysis of Dewar-acetophenone to this molecular feature. With **1b**–**2b**, on the other hand, both the S_1 and T_1 states of the product are $\pi\pi^*$ in nature,[3,5] and therefore, the present system is expected to be devoid of this dislocation. Because of the latter feature (ii), chemiexcitation of **2b** should lead to the formation of **3**, and hence the non-adiabatic fraction in the thermal reaction of **1b** could be detected directly by product analysis for **3**. For comparison, the parent Dewar-anthraquinone (**1a**) was synthesized and its isomerization to anthraquinone was also studied.

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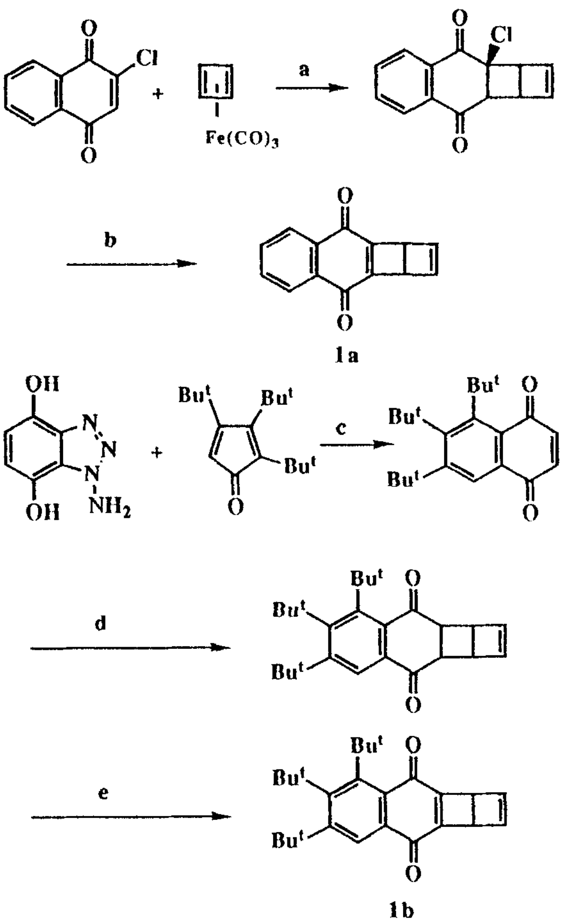
Dewar-anthraquinones **1a** and **b** were synthesized according to Scheme 1. Attempt to purify **1a** resulted in rearrangement to **2a**. However, samples of **1a** used in the study contained **2a** as a sole impurity detectable by NMR, and the amount of the contaminant was taken into account in determining the thermodynamic parameters for the isomerization of **1a**. **1a**: ^{1}H NMR ($CDCl_3$), δ (ppm) 8·10–8·00 (m, 2H), 7·74–7·63 (m, 2H), 6·65 (br s, 2H), 4·48 (br s, 2H). Tri-*tert*-butyl derivative, **1b** was purified by preparative thin-layer chromatography (TLC) with development at −15 °C. **1b**: ^{1}H NMR ($CDCl_3$) δ (ppm) 7·60 (s, 1H), 6·64–6·54 (m, 2H), 4·47–4·32 (m, 2H), 1·43 (s, 18H), 1·37 (s, 9H). In the synthesis of **1b**, special precautions were taken to prevent photolysis of reaction materials by ambient light, and all the synthetic procedures were performed in a dark room under a red safety lamp.



a; $Ce(NH_4)_2(NO_3)_6$, b; $LiN(i\text{-}Pr)_2$/-15°C, c; $Pb(OAc)_4$, d; Cyclobutadiene iron tricarbonyl / $Ce(NH_4)_2(NO_3)_6$, e; 1) $LiN(i\text{-}Pr)_2$, 2) NBS /-70°C

Scheme 1

NMR analyses revealed that the thermolyses of **1a** and **1b** gave the corresponding anthraquinones, **2a** and **2b**, in 99% yields. The reactions of **1a**, and **b** were followed kinetically in dichloromethane by measuring electronic spectra using a temperature-regulated UV cell. The disappearance of **1** and the appearance of **2** were first-order reactions. Rate constants at various temperatures and activation energies are summarized in Table 1. Reaction enthalpies for the cycloreversion of **1** were estimated based on the exothermic heat flow obtained by differential scanning calorimetry.

As shown in Table 1, thermolyses of **1a** and **1b** release 89 and 74 kcal mol^{-1} (1 kcal = 4·184 kJ), respectively, in activation enthalpy and reaction enthalpy. These amounts of energy are sufficient to produce either singlet or triplet states of the products **2a** and **2b**.

In order to detect excited-state production in the thermolysis of **1a**, the 'chemical titration technique'[4] was employed by using *trans*-stilbene as an indicator because the anthraquinone triplet is known to effect the isomerization of *trans*-stilbene to *cis*-stilbene.[6] Moreover, since intersystem crossing in anthraquinone is a very fast process, determination of the triplet yield of anthraquinone should suffice to measure the total yield of excited-state products. A benzene solution of **1a** (0·1 M) and *trans*-stilbene (0·01 M) was degassed, thermolysed and analysed for *cis*-stilbene formation. However, no *cis*-stilbene formation was observed. In the case of tri-*tert*-butylanthraquinone (**2b**), its triplet energy of *ca* 55 kcal mol^{-1} (Ref. 5) does not suffice to excite *trans*-stilbene. In this case, however, molecular rearrangement to give **3** could be available as a measure of the population of the excited state which is responsible for the formation of **3**. Thus, careful analyses of the thermolysate of **1b** revealed the formation of a detectable amount of **3** in the thermolysis of **1b**.

In a practical run, a solution of 0·5 g of **1b** in dichloromethane was thermolysed at room temperature, where product **3** possesses a lifetime long enough for product analysis.[3] The reaction mixture was subjected to silica gel TLC on a preparative scale at −15 °C. The band fraction containing **3** was collected and dissolved in 0·5 ml of dichloromethane, and the solution obtained was quantitatively analysed for **3** by high-performance liquid chromatography. Three replicate experiments revealed the formation of **3** in an average yield of 0·049% with a standard deviation of 0·008%. Based on this value and the quantum yield of 0·01 for the photovalence isomerization in equation (2), it was concluded that the thermal cylcloreversion of **1b** was accompanied by a non-adiabatic fraction of not less than 0.4%. All of the photovalence isomerizations of aromatic molecules known

Table 1. Rate constants, activation energies and reaction enthalpies for the thermal rearrangement of **1a** and **b** to **2a** and **b**

Reaction	Temperature (°C)	Rate constant[a] (10^5 s^{-1})	Activation energy[a] (kcal mol^{-1})	Reaction enthalpy[b] (kcal mol^{-1})
1a–2a	0	2·98 ± 0·36	26·7 ± 1·5	64
	10	27·5 ± 1·2		
	20	91·8 ± 3·0		
2a–2b	3·1	2·22 ± 0·07	18·2 ± 1·2	55
	8·3	4·18 ± 0·15		
	12·3	6·60 ± 0·23		

[a] Measured in dichloromethane solutions. All rate constants and activation energies are least-squares values, all errors are standard deviations.

[b] Measured by differential scanning calorimetry on samples in diphenyl ether solutions.

so far generally involve an excited singlet state and not a triplet state.[7] Further, the reaction in equation (2) could not be quenched by triplet quenchers such as anthracene and oxygen. Hence it is likely that thermal cycloreversion of **1b** gives the excited singlet state of **2b**. The present system represents the first example of a simple unimolecular electrocyclic reaction to populate the singlet excited state of the product. Although there is a possibility of the existence of chemiexcitation to give the triplet **2b**, this remains to be studied owing to our lack of methods to detect the triplet state. Further studies including a theoretical treatment of the reaction are in progress.

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